The University of Chicago

THE RELATIVE INTENSITIES OF MERCURY LINES UNDER DIFFERENT CONDITIONS OF EXCITATION

A PART OF THE DISSERTATION SUBMITTED
TO THE GRADUATE FACULTY IN CANDIDACY
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF PHYSICS

By

MARCEL JULES EDWARD GOLAY

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THE RELATIVE INTENSITIES OF MERCURY LINES UNDER DIFFERENT CONDITIONS OF EXCITATION

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Abstract

The relative intensities of the lines of the $2s-2p_i$ triplet have been measured by a photographic method with a calibrated tungsten lamp as a standard of comparison. The intensity ratios have been found to vary with conditions of excitation due to the absorption of the 5461 and 4047 lines by atoms in the metastable states $2p_1$ and $2p_3$. About three-quarters of the 5461 radiation and about one-third of the 4047 radiation were absorbed in a commercial mercury-filled tube with three electrodes when a high plate current was passed through the tube. A lesser absorption was found when an ordinary arc was used and when small plate currents were passed in the three-electrode tube. A tube specially built to excite mercury by electronic bombardment and provided with means for controlling the mercury pressure gave uniform results under various conditions of mercury pressure and plate current, and the double ratio of 8.5:3.3:1 was found for the intensities divided by the fourth powers of the corresponding frequencies. The ratio of 4078:4047 was found to vary with plate voltage in a manner similar to the variation of efficiency of ionization with electron velocity. It was attributed to the presence of two mechanisms of emission giving widely different intensity ratios, namely, excitation of the neutral atom to a higher energy level, and recombination of the ionized atom. A roughly quantitative survey of the intensities of the excitation and of the recombination spectra indicated that in comparison with atoms excited to a higher level by electronic impact as occurs in the arc, recombined atoms will prefer the singlet to the triplet system, while within each system their order of preference is P, S, D, and p, s, d, respectively. Also, within each state, a level at about the height of the $4S$ level is preferred to the others.

General

THE purpose of the research reported here was primarily the study of the $2s-2p_i$[1] triplet. The intercombination line $2S-2p_2$ of wave-length 4078 was also included in this study because of the work of Houston,[2] who treats the lines $2S-2P$, $2S-2p_2$, $2s-2P$ and $2s-2p_i$ (i=1, 2, 3) as a whole. According to this author the ratio 5:3:1 must be found for

$$\frac{A(5461)}{N_3}:\frac{A(4358)}{N_3}+\frac{A(4078)}{N_1}:\frac{A(4047)}{N_3},$$

where A designates the intensity divided by the fourth power of the frequency and N the number of atoms in the respective initial states. The quantities written above are proportional to the squared amplitudes of the corresponding lines, and it is for these squared amplitudes that the "sum-rule" must hold.

[1] Notation of Paschen.

[2] W. V. Houston, Phys. Rev. **33**, p. 297 (1929).

The squared amplitudes of the individual lines can also be determined from the formulas given by Houston. They give approximately the ratio 5:2.9:1 for the relative intensities of the triplet lines, divided by the fourth powers of the corresponding frequencies. They also give the ratio of 0.1:1 for the lines 4078 and 4047. This signifies that for an equal population of their respective initial levels, line 4078 will have approximately one-tenth the intensity of line 4047, the relative intensities of these two lines giving thus a basis for a computation of the relative population of their respective initial levels.

Method of Intensity Measurements

When two lines are but a few angstroms apart in wave-length, their relative intensities may in principle be measured by weakening one line by a known amount until it has the same intensity as the other, that is, until the blackening of the photographic plate is the same for the two lines. Usually both lines are weakened by a series of absorbing screens, and their relative intensities are obtained through some process of interpolation which affords at the same time a number of results, which must verify each other, when the image of the weaker line through the clearer weakeners is comparable in intensity to the image of the stronger one through the more opaque portions.

When the lines to be compared are sufficiently separated to warrant a determination of the sensitivity of the emulsion for the corresponding wave-lengths, a source of known spectral distribution such as a black body or an incandescent filament of known temperature and emissivity is used for this purpose. Each line is then compared with the continuous radiation of the same wave-length. This can of course be done as before, by means of weakeners, calibrated for each of the different wave-lengths of the group under study.

Their use, however, can be avoided very simply by using the standard of comparison to put on the plate a series of intensity marks of known relative intensities. As the standard of comparison emits a continuous spectrum, the gradation of intensities can be obtained by varying the width of the slit, and if a lens is used to focus on the slit an image of the tungsten ribbon of the lamp used as a standard, one can also place diaphragms of known geometrical transmission in front of the lens.

A lower limit for the slit-width is set by the accuracy with which this width can be measured, and by the size of the diffraction pattern formed on the prism. It is desirable that the main fringe and at least one or two lateral fringes appear on the prism when sighting it from the camera side of the spectrograph, in order to avoid losing more than a few percent of the light. Conversely, the largest slit-width must not allow the integrated spectrum thus obtained to misrepresent the intensity of the source, and the sensitivity of the emulsion. According to Ornstein no errors due to the integration of the spectrum will be appreciable if the width of the slit corresponds to less than 60A on the plate for any of the wave-lengths studied.

The diaphragms placed in front of the lens must cover enough of the latter so that a full image of the uncovered portion can be seen on the prism from

the camera side, while if but little light is desired, these diaphragms must have holes not small enough to create on the slit a main fringe equal in width to the difference between the image of the filament and the opening of the slit.

When a set of intensity marks has been put on a plate it is necessary to take only one spectrogram of the source of light, taking care to use a rather wide slit, and to compare the lines with the comparison spectrum at the same wave-length. One can thus take many exposures on one plate, which is advantageous when studying the variations of relative intensity with certain conditions of experimentation. One obtains indeed but one figure for every exposure, while several are obtained when the source is photographed through a series of weakeners. If it is desired to obtain a few figures for every condition of light emission studied, one has to take as many exposures, preferably using various diaphragms in front of the lens projecting an image of the source on the slit.

In the work reported here, care was taken that light from all sources photographed followed the same optical path. As an added precaution it was

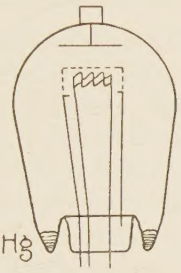

Fig. 1. Diagram of mercury-filled tube.

also verified that the transmission of the whole optical system was sensibly the same along the optical axis and away from this axis.

As sources of known radiation incandescent lamps with a flat tungsten ribbon were used and their temperatures determined photographically by comparison with a standard of known temperature and emissivity, supplied to Ryerson Laboratory by Dr. Forsythe of Nela Park. The secondary standards were generally operated at 2780 to 2800°K, and the time of exposure was the same for the standard and for the spectrum studied, to avoid errors due to a difference in Schwarzchild's constant for different wave-lengths. The radiation emitted by the standard lamp was calculated from the black body radiation formula. Corrections for the emissivity of tungsten at 2800°K at various wave-lengths were introduced. Corrections were also introduced for the dispersion of the spectrograph and for a difference in broadness of the lines due to different distances of the plate from the camera lens.

Sources of Light and Results, $2s - 2p_i$ Triplet

Some preliminary measurements were carried out, with a home-made arc, a Cooper-Hewitt arc, and a mercury-filled tube, obligingly furnished by the Bell Telephone Laboratories. Fig. 1 shows a schematic drawing of this tube.

The spectrum of the ordinary arc was photographed at various time intervals, beginning at the moment the arc was started, and continuing until the steady state was attained. It was then observed that the ratio of 5461:4047 increased from about 4 to about 7, while the ratio of 4358:4047 decreased from about 5 to about 3. Similar results were obtained for the Cooper-Hewitt arc. Table I shows a set of results obtained similarly for the tube furnished by the Bell Telephone Laboratories, by observing the white streaks emerging from the grid at a potential just sufficient to maintain an arc.

TABLE I *I/ν^4 values for lines from tube shown in Fig 1.*

Condition of tube	5461:4047[3]	4358:4047
First exposure, tube cold	5.1	3.7
	5.6	3.7
	5.8	3.8
	6.8	3.6
	7.4	3.5
	7.3	3.4
Last exposure, tube hot	7.4	3.4

The results to be discussed later suggest the following explanation of these figures. It will be shown that the true intensity ratio is about 8.5:3.3:1. The lines 5461 and 4047 are, however, absorbed by the atoms in the metastable states $2p_1$ and $2p_3$. As the line 4358 terminates on the level $2p_2$ where the strong resonance line 2537 originates, it seems plausible to assume that the population of the $2p_2$ level is not large enough to cause any appreciable absorption of the line 4358. The population of the metastable states is roughly proportional to the ratio of the rate at which these states are reached by the excited atoms, to the rate at which they leave them owing to collisions of the second kind. The rate at which atoms are sent into metastable states is roughly proportional to the current, while the rate at which they leave them increases with the number of collisions per unit time; this number increases about linearly with the temperature, and the density, this latter quantity rising rapidly with the temperature. It can therefore be expected that at a low pressure, the ratio of 5461:4047 will be considerably reduced, line 5461 being much more absorbed than line 4047 on account of the greater population of the state $2p_1$, while the ratio of 4358:4047 will be found somewhat too high on account of the absorption of line 4047. As the temperature and the pressure increase these ratios will approach their true values, due to the diminished population of the metastable states, as can be verified in the above table.

The following tables show a typical set of results susceptible of similar interpretation. The temperature of the tube was kept approximately constant during the observation. The time of exposure for the spectrum and for the standard light was the same for each plate. Diaphragms were placed in front of the condensing lens to reduce the very different intensities photographed to approximately the same level of blackness on the plate.

[3] All ratios given in this article refer to the intensities divided by the fourth powers of the frequencies.

TABLE II. *I/ν^4 ratios for constant tube temperature but varying plate current.*
(Observation of light emitted between grid and plate)

Plate current	5461:4047	4358:4047
1.0 amp.	3.2	
1.0	3.6	4.9
0.27	5.9	4.4
0.27	5.0	4.3
0.0075	8.1	4.0
0.0065	7.9	3.9
0.0055	8.3	3.9
0.004	9.0	3.7

The explanation of these results is obvious. A higher plate current increases the rate at which atoms are thrown into metastable states, and higher absorption of line 4047, and especially of line 5461, results therefrom.

From the foregoing it appears that the Hg density affects the results in a two-fold manner. A direct effect of higher density would be a more rapid elimination of the metastable states, thus reducing the effect of absorption in the intensity ratios. This first effect would be masked, however, by the more complicated and more intense phenomena accompanying high pressures.

Determination of the true intensity ratios of the triplet. The facts mentioned above were not apparent at the time these experiments were carried out, for it was expected that the ratio 5:3:1 would be found for the relative intensities of the triplet divided by the fourth powers of the frequencies, and ratios higher than 5 for lines 5461 and 4047 could not be explained by an absorption of line 5461. At the same time it was obvious that the absorption of line 4047 was much less than the absorption of line 5461, for the population of the $2p_1$ state is much larger than the population of the $2p_3$ state, and this theoretical prediction was confirmed by the comparatively smaller variations of the ratio of 4358:4047. Also, the glass of the three-electrode tube used was not very clear, and had a larger transmission for the 5461 line than for the other lines of the triplet.

A tube was then built, with means for controlling the Hg pressure, and with a quartz window for the eventual study of the ultraviolet lines.

This tube is shown in Fig. 2. Electronic emission was provided by a tungsten filament. The leads into the tube were tungsten rods, while the other metallic portions were of nickel. A plate, P, with a rectangular hole cut to correspond to the opening, A, of the cage was inserted as shown in the figure, to prevent the white light of the filament from reaching the slit of the spectrograph. A number of spectra were taken with the end, B, of the cage open, so that a considerable amount of light due to the blue glow filling the tube contributed to the radiations photographed. Any amount of shielding in the far end of the tube failed to eliminate this glow. As it was thought that this glow was due to a somewhat different mode of excitation from that which produced the light in the cage by electrons of a definite velocity, the far end of the cage was subsequently closed, as shown in the figure. This was done by means of a little strip of platinum, blackened in the flame of a match. A

small strip of nickel, C, was welded over the far end of the grid to prevent a direct illumination of this end wall by the filament. At the time this change was effected, the nickel grid of rather coarse mesh, hitherto used, was replaced by a nickel grid of the finest mesh obtainable. This was done for the purpose of obtaining a more uniform flow of electrons in the cage, and surprisingly enough this new grid stood higher currents than the coarse one formerly used, without showing any trace of deterioration. In spite of the electrical screening provided by the shield, S, and the front plate, P, the space, F, in the front end of the tube was filled with a weak glow, the part of this glow in the prolongation of the cage contributing, therefore, to the light photographed.

The Hg pressure in the tube was indirectly controlled by placing the Hg trap in a beaker of water of a certain temperature.

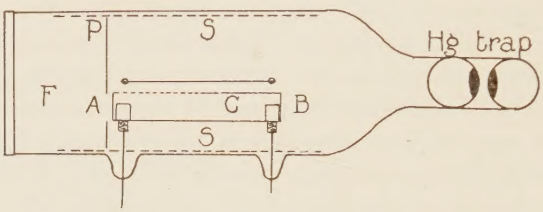

Fig. 2. Diagram of apparatus.

A thorough baking out of the tube was found necessary to avoid nitrogen and carbon monoxide bands. This was done by wrapping asbestos around the tube and letting a plate current of 0.8 to 1 amp. flow under a potential of about 200 volts for a few hours. Even though the CO bands were observable at the end of this period, they would quickly disappear after the asbestos had been removed and the tube brought to its normal running temperature.

A few refinements were introduced in the method of intensity measurements. They are outlined below.

A little strip of gray glass was placed in the camera on the path of line 4358, in order to bring this line to the same blackness level as lines 4047 and 5461. As this line and the standard radiation for its measurement were both modified in the same manner, no change was called for in the method of measurement. While more accurate, the results thus obtained for the 4358:4047 ratios agreed well with a number of results obtained before this precaution was taken. About 40 exposures were taken on each plate, a little less than half this number being assigned to the intensity marks. Two was chosen for the ratio of the geometric progression of intensities, and two or three exposures were taken for each intensity, the slit width and the number of holes used in the diaphragm being both varied so as to check the method used, and to reduce chance errors due to setting and variations in the emulsion. (The different measurements of blackness for marks of the same theoretical intensity proved to be closely grouped in the great majority of cases.) Also, each condition of plate current and plate voltage studied was photographed two

or three times, as the light intensity permitted, using the diaphragm with maximum openings, and others of one-half and one-quarter the area of the first. As a last precaution, all plates were wiped continuously while in the developer, to insure uniformity of development.

Two current values, 0.3 and 0.6 amp. were used under various voltages to bring out any systematic dependence of the intensity ratios observed upon the plate current, as well as to bring out any voltage dependence for any one fixed current, especially with reference to the 4078:4047 ratio.

The narrow range of Hg temperature explored (limited for the high temperature by the coolest point of the tube to avoid condensation in this point, and for the low temperature by the light intensity fit for convenient exposures) was considered wide enough to detect any dependency upon pressure on account of the comparatively large range of pressures corresponding to these temperatures.

No dependence upon plate current, plate voltage and Hg pressure was found for the relative intensities of the triplet, while the ratio of 4078:4047 showed a marked dependency upon plate voltage.

The averages obtained for the triplet are given in Table III.

TABLE III. *I/v^4 values for triplet lines obtained with tube shown in Fig. 2.*

Plate No.	Temp. of Hg	4358:4047	5461:4047
14	100°C	3.3	8.3
22	0	3.0	8.5
23	22	3.3	8.5
"	60	3.4	
25	20	3.2	7.8
29	20	3.2	8.8
"	40	3.3	7.9
30	40	3.4	7.9
31	22		9.2
34	23		8.8
35	41.5	3.3	8.6
36	25		9.5
37	24		8.5
		Average 3.3	8.5

The experimental error attached to the average given for the ratio of 5461:4047 is probably larger than for the other one, but should not exceed 10 percent, assuming, however, that the temperature of the lamp used as standard is correct.

RATIO OF 4078:4047 AND GENERAL STUDY OF THE ELECTRONIC BOMBARDMENT EMISSION

As mentioned above, the ratio of 4078:4047 varies with plate voltage. This is shown in Fig. 3, where this ratio has been plotted as a function of the plate voltage from the data obtained from five plates. These curves point to a rapid rise to a maximum, reached at about 100 volts, and then a slow downward trend.

The existence of a variation in relative intensity of two lines makes it necessary to assume the operation of at least two different mechanisms—if there were only one, the absolute intensity might vary, but not the relative. Each of these mechanisms will presumably be operative in producing both lines, but with a different ratio of intensities. The ratio measured will be some weighted average of the ratios which are characteristic of each of these mechanisms.

This variation with voltage is strikingly similar to the variation of the efficiency of ionization as found by a number of authors. For the purpose of comparison, the probability of ionization of mercury atoms by electrons has been plotted as the dotted curve. It was obtained from Bleakney's[4] data by adding the ordinates of his curves for the probability of single, double, and triple ionization. It also represents the variation in the intensity of the light due to atoms which have been ionized and recombined with electrons if it be

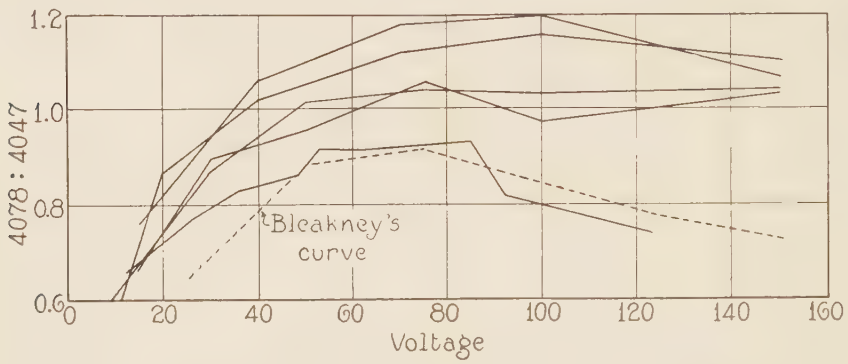

Fig. 3. Ratio 4078:4047 plotted as a function of the plate voltage from data obtained from five plates.

assumed that doubly and triply ionized atoms recapture successively, two and three free electrons respectively from the negative space charge inside the cage.

The parallelism of this curve with the ratio of 4078:4047 seems to suggest the following explanation. Atoms which have been previously ionized will emit a recombination spectrum with a comparatively larger ratio of 4078: 4047 than excited atoms, while the observed ratio will vary somewhat parallel to the amount of light emitted which is due to recombined atoms, if the number of excited atoms is assumed to have no variations, as marked as the one shown by Fig. 3, beyond the ionization potential. This explanation would be supported by the fact that many ionized Hg lines were quite conspicuous at the higher voltages used (40 volts and above), while the presence in the cage of slow secondary electrons made conditions favorable for the recombination of Hg ions.

If the large differences found between the intensity distributions in an

[4] Bleakney, Phys. Rev. **33**, 139 (1930).

ordinary arc and in an electronic bombardment spectrum were attributed to the presence in the latter of a recombination spectrum certain consequence would follow which are brought out by Table IV. This table has been prepared from a table giving the intensities of the lines in an electronic bombardment spectrum at 70 volts using the intensities of the lines of an arc spectrum as units. All the values obtained for lines originating at a certain level have been averaged, and these averages have been given in Table IV. This table therefore gives an estimate of the population of the various levels in an electronic bombardment spectrum in comparison with an arc spectrum. According to what has been said above Table IV would indicate that by comparison

TABLE IV. *Relative population of levels—electronic bombardment—spectrum vs. arc spectrum.*

Level	Relative Population	Level	Relative Population
$2S$	1.5	$2s$	0.15
$3S$	3.	$3s$	0.15
$4S$	11.	$4s$	0.8
$5S$	4.	$5s$	0.4
		$6s$	0.15
$4P$	55.		
$5P$	25.	$4p_1$	0.6
$6P$	2.	$5p_1$	1.4
$7P$	1.5	$6p_1$	0.6
$3D$	0.4	$3d_1$	0.14
$4D$	2.2	$4d_1$	0.15
$5D$	1.7		
$6D$	0.4	$3d_2$	0.16
$7D$	0.2	$4d_2$	0.3
$8D$		$5d_2$	0.8
		$3d_3$	0.2
		$4d_3$	0.1

with excited atoms, recombined atoms will occupy a much larger proportion of singlet terms, while within each system of terms the P-state (or the p-state), and within each state a level at about the height of the $4S$ level would be most favored in this new population distribution.

This explanation for the variation of the ratio of 4078:4047, and the consequences of this explanation, are given with much reserve, however, as it has been the conclusion reached by F. L. Mohler[5] and other authors that in a recombination spectrum the triplet terms are comparatively more populated than in an excitation spectrum.

The writer wishes to express his appreciation to Professors Monk and Eckart for the suggestion of the problem and assistance throughout the duration of the work.

[5] F. L. Mohler, Phys. Rev. Suppl. **1**, 221 (1929).